

AC and DC conductivity correlation: the coefficient of Barton–Nakajima–Namikawa relation

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Abstract

It has been some time since an empirical relation, which correlates DC with AC conductivity and contains a loosely defined coefficient thought to be of order one, was introduced by Barton, Nakajima and Namikawa. In this work, we derived this relation assuming that the conductive response consists of a superposition of DC conductivity and an AC conductivity term which materialized through a Havriliak–Negami dielectric function. The coefficient was found to depend on the Havriliak–Negami shape parameters as well as on the ratio of two characteristic time scales of ions motion which are related to ionic polarization mechanism and the onset of AC conductivity. The results are discussed in relation to other relevant publications and they also applied to a polymeric material. Both, theoretical predictions and experimental evaluations of the BNN coefficient are in an excellent agreement, while this coefficient shows a gradual reduction as the temperature increases.

Keywords: AC conductivity, DC conductivity, ionic conductors, ionic polarization mechanism, BNN relation

1 Introduction

Nearly four decades ago, an empirical relation was introduced by Barton, Nakajima and Namikawa which is known as BNN relation [1, 2, 3]. This expression correlates the electrical conductivity to the dielectric strength of the lower frequency polarization mechanism through,

$$\sigma_0 = p\varepsilon_0\Delta\varepsilon\omega_{max} , \quad (1)$$

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where p is a loosely defined parameter, expected to be of order 1, σ_0 is the apparent DC conductivity, $\Delta\epsilon$ is the dielectric strength, ω_{max} is the angular frequency which corresponds to the maximum value of dielectric losses and ϵ_0 is the permittivity of vacuum. The loss peak which associated to $\Delta\epsilon$ is, in general, characterized as broad. $\Delta\epsilon$ may arise entirely from mobile charge effects and not involve bulk dielectric effects at all. When Eq. (1) is satisfied, both AC and DC conductivity may arise from the same type of charge transport mechanism [4, 5].

The BNN relation has played an important role in the analysis and the treatment of frequency response dielectric data [6, 7, 8, 9, 10, 11], assuming that $p \sim 1$ with most of the corresponding works dealing with the scaling and universality issues of AC conductivity. In the literature a large number of different conductive disordered materials have been found to satisfy Eq. (1). The BNN relation is valid not only in amorphous solids, ionic glasses, single crystals and polymers but also in a variety of other materials such as microporous systems [12] and proteins in hydrated state [13]. The reported values of the coefficient p vary significantly, about three orders of magnitude from less than one up a few hundred [1, 2, 3, 4, 5]. However, for a variety of materials, the p value falls mostly in the range from 0.5 to 10 [14], while in the majority of the cases the p value is near unity, as it is shown as well in Fig. 3 of Ref. [9].

The factors affecting the accurate estimation of p value are discussed in Refs. [14, 15]. However, some aspects should be mentioned here which are related to the electrode effects. In the case of fully-blocking electrodes, if the data do not extend to the region where $\sigma'(\omega)$ decreases towards zero in the lower-frequency plateau, the result might not define the DC conductivity accurately. In the case of partial-blocking electrodes behavior two regions of constant $\sigma'(\omega)$ values could possibly appear [16]. In such cases it could be possible that the higher-frequency plateau region would lead to a more plausible p estimate than the lower-frequency one, even though the latter is considered as the DC conductivity [16].

In the various models, which have been proposed for the description of the dielectric response of disordered conductive materials, the BNN relation has been used as a testing equation through the calculation of p coefficient [7, 9, 17, 18]. The value of p is definitive, in order one to classify conductive materials. According to Hunt [19], the role of Coulomb interactions in the derivation of the BNN relation is of great importance, while the non-universality of the high frequency limit of the AC conductivity is incompatible with a universality in the BNN relation [20]. However, various models proposed for a particular kind of materials such as ionic glasses and disordered conductors, give universal values for the BNN coefficient p . Dyre [7] obtains a value of $p = 0.42$ by using the random energy barrier model. In a subsequent work Dyre and Schröder [9] reported a value of $p = 1.5 \pm 0.4$ for the simulation of the symmetric hopping model in the extreme disorder limit. It has been pointed out by Macdonald [6] that the K1 conducting-system model could lead to a quantitative value for p , which depends on the value of β_{1C} of the Kohlrausch-Williams-Watts (KWW) stretched exponential response function. For ion-conducting homogeneous glasses and single crystals with charge motion allowed in all three dimensions, it has been shown that the only possible value is $\beta_{1C} = 1/3$ and the resulting high frequency limiting response power law exponent is equal to $2/3$ [18]. According to these values, the BNN coefficient has a universal value of $p = 1.65$, while in the framework of the K1 model, as $\beta_{1C} \rightarrow 1$, p should also approach unity in the limit. In a recent paper Macdonald [15] has provided a detailed analysis and p estimates for the variety of conductive-system models. These models involving a single fractional exponent, for an appreciable range of exponent values, show that the p values are quite near 1.

A modified BNN relation has been suggested by Dygas in [21]. It is proposed that the values of modified P coefficient are related to the spatial extent and time scale of nonrandom local hopping of charge carriers. It also gave an expression of the BNN coefficient in the case of Cole–Cole dielectric behavior of ionic polarization mechanism.

The BNN equation quantifies the relation between short range and long range ions motion of the AC response of conductive materials. To be specific the p coefficient reflects a measure of the correlation between AC and DC conductivity. In the present work, we will attempt to derive the BNN coefficient based on impedance spectroscopy formalism, as well as on widely used phenomenological and empirical relations and to discuss the results with relevant published works. The exact knowledge of the parameters on which the p coefficient depends, is of great importance, not only from the fundamental point of view, but also for applications, because this could lead to design and development of a variety of materials with predetermined dielectric and electrical properties.

2 Theoretical considerations

The complex conductivity $\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega)$ is connected to the total complex dielectric constant $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ via the following relation

$$\sigma^*(\omega) = j\omega\varepsilon_0\varepsilon^*(\omega) . \quad (2)$$

In the above relation, if the contribution of the DC conductivity, σ_0 , is subtracted from $\varepsilon^*(\omega)$, then

$$\sigma^*(\omega) = \sigma_0 + j\omega\varepsilon_0\varepsilon_d^*(\omega) , \quad (3)$$

where $\varepsilon_d^*(\omega)$ represents the complex dielectric constant caused only from the dynamic conductivity.

In ionic materials, the description of the real part of complex conductivity spectra in the low frequency regime, below 100 MHz, and in the absence of electrode polarization effects, is given by the equation [22, 23, 24, 25, 26]

$$\sigma'(\omega) = \sigma_0 \left[1 + \left(\frac{\omega}{\omega_0} \right)^n \right] , \quad (4)$$

where n (with $0 < n < 1$) is a constant. The characteristic frequency ω_0 corresponds to the onset of AC conductivity. At this frequency, the real part of complex conductivity becomes twice to that of the DC conductivity, $\sigma'(\omega_0) = 2\sigma_0$. This last equation has been introduced in Ref. [27], in order to describe crystals with defects and an activated number of charge carriers. Eq. (4) cannot be taken as a model relation, because it is not able to reproduce the individual AC response characteristics which are derived from other functions of impedance spectroscopy (i.e. the peak and the dielectric strength, in $\varepsilon^*(\omega)$ formalism when ionic dispersions take place). Eq. (4) is considered as a relation which approximates well only the frequency dependence of the real part σ' , since at low frequencies, σ' describes the DC conductivity plateau of AC response, while at high frequencies, σ' describes the well-known Jonscher power law behavior [28]. In general, depending on the individual characteristics of $\varepsilon_d''(\omega)$ responses, Eq. (4) can or cannot describe satisfactorily the function $\sigma'(\omega)$ at the onset region.

If we assume that the real parts of Eqs. (2), (3) and Eq. (4) are equal not only at the high frequency limit but also at $\omega = \omega_0$, then in these cases, from Eqs. (2), (3) and (4) with $\omega = \omega_0$ we find

$$\sigma_0 = \varepsilon_0 \omega_0 \varepsilon''(\omega_0)/2 \quad (5)$$

and

$$\sigma_0 = \varepsilon_0 \omega_0 \varepsilon_d''(\omega_0) . \quad (6)$$

So, in these cases the characteristic frequency ω_0 , should be defined also as the frequency at which the losses from the DC conductivity are equal to the respective ones of the dynamic conductivity, since $\varepsilon''(\omega_0) = 2\varepsilon_d''(\omega_0)$.

3 The BNN relation

In what follows, let us consider that, the conductive response of a disordered material in the frequency spectrum under study, is characterized only by the existence of DC conductivity and an AC conductivity term. The latter is considered that includes entirely contribution due to mobile ions effects. These effects should lead to the appearance of a polarization mechanism in ε^* formalism, which should take place around the onset frequency ω_0 , with loss peak frequency, ω_{max} , and strength $\Delta\varepsilon$. The real part of complex conductivity should be given by using Eq. (3), as follows

$$\sigma'(\omega) = \sigma_0 + \varepsilon_0 \omega \varepsilon_d''(\omega) . \quad (7)$$

The $\varepsilon_d''(\omega)$ should be considered as $\varepsilon''(\omega)$ conductive-system values, while for its description the well known and widely used Havriliak–Negami (H–N) empirical dielectric function is used here as well [29],

$$\varepsilon_d''(\omega) = \frac{\Delta\varepsilon \sin(\beta\phi)}{[1 + 2(\omega/\omega_{HN})^\alpha \cos(\alpha\pi/2) + (\omega/\omega_{HN})^{2\alpha}]^{\beta/2}} \quad (8)$$

where

$$\phi = \arctan \left(\frac{(\omega/\omega_{HN})^\alpha \sin(\alpha\pi/2)}{1 + (\omega/\omega_{HN})^\alpha \cos(\alpha\pi/2)} \right) . \quad (9)$$

The shape parameters take values in the range $0 < \alpha, \beta \leq 1$ and are closely related to the slopes in $\log \varepsilon_d''$ vs. $\log \omega$ plots ($\varepsilon_d'' \sim \omega^\alpha$ at $\omega \ll \omega_{max}$ and $\varepsilon_d'' \sim \omega^{-\alpha\beta}$ at $\omega \gg \omega_{max}$). It should be mentioned here, that there exist models which have been proposed for the interpretation of the limiting behavior of the H–N relaxation function, a behavior that is related to the slopes α and $-\alpha\beta$ [30, 31]. The limiting case of $\alpha = \beta = 1$ corresponds to Debye behavior with a single relaxation time $\tau = 1/\omega_{HN}$. The frequency ω_{HN} is related to ω_{max} through

$$\omega_{max} = A\omega_{HN} , \quad (10)$$

where

$$A = \left(\frac{\sin(\alpha\pi/(2\beta+2))}{\sin(\alpha\beta\pi/(2\beta+2))} \right)^{1/\alpha}. \quad (11)$$

The total dielectric losses should be written as

$$\varepsilon''(\omega) = \varepsilon_d''(\omega) + \varepsilon_c''(\omega), \quad (12)$$

where $\varepsilon_c''(\omega)$ stands for the losses due to the DC conductivity, σ_0 . So, from the real part of Eq. (3) we get $\sigma_0 = \varepsilon_0\omega\varepsilon_c''(\omega)$. At frequency $\omega = \omega_0$ and with the assumption that the real part of Eqs. (3) and (4) are equal at $\omega = \omega_0$, the relation $\varepsilon_c''(\omega_0) = \varepsilon_d''(\omega_0)$ holds (see Eq. (6)). Therefore the relation $\sigma_0 = \varepsilon_0\omega_0\varepsilon_d''(\omega_0)$ will be valid and with the help of Eqs. (8) and (9) we arrive at the BNN relation $\sigma_0 = p\varepsilon_0\Delta\varepsilon\omega_{max}$ where the BNN coefficient is equal to

$$p = \frac{\omega_0}{\omega_{HN}} \left(\frac{\sin(\alpha\beta\pi/(2\beta+2))}{\sin(\alpha\pi/(2\beta+2))} \right)^{1/\alpha} \times \frac{\sin(\beta\phi)}{[1 + 2(\omega_0/\omega_{HN})^\alpha \cos(\alpha\pi/2) + (\omega_0/\omega_{HN})^{2\alpha}]^{\beta/2}}, \quad (13)$$

where in this last expression ϕ is given through Eq. (9) at $\omega = \omega_0$, while in Cole–Davidson case ($\alpha = 1$) takes its simplest form, $\phi = \arctan(\omega_0/\omega_{HN})$.

At the high frequency limit, $\omega \gg \omega_{HN}$, Eq. (8) is given by

$$\varepsilon_d''(\omega) \cong \Delta\varepsilon \sin(\alpha\beta\pi/2)(\omega/\omega_{HN})^{-\alpha\beta},$$

while Eq. (9) becomes $\phi = \alpha\pi/2$ and Eq. (7) is written as

$$\sigma'(\omega) \cong \sigma_0 + \varepsilon_0\omega_{HN}\Delta\varepsilon \sin(\alpha\beta\pi/2)(\omega/\omega_{HN})^{1-\alpha\beta}. \quad (14)$$

The function $\sigma'(\omega)$ as given by Eqs. (4) and (14), in the high frequency limit of these two equations, $\omega \gg \omega_{HN}$, should be the same. This means that the power law exponent of high frequency limit is $n = 1 - \alpha\beta$, while

$$\omega_0^n = \frac{\sigma_0}{\varepsilon_0\Delta\varepsilon \sin(\alpha\beta\pi/2)} \omega_{HN}^{n-1} \quad (15)$$

holds as well. The previous relations Eqs. (14) and (15), coincide with the ones in Ref. [21], where similar expressions have been derived previously. Then based on Eq. (15) and with the use of Eqs. (1), (10) and (11) the BNN coefficient should be expressed as

$$p = \left(\frac{\omega_0}{\omega_{HN}} \right)^{1-\alpha\beta} \sin\left(\frac{\alpha\beta\pi}{2}\right) \left(\frac{\sin(\alpha\beta\pi/(2\beta+2))}{\sin(\alpha\pi/(2\beta+2))} \right)^{1/\alpha}, \quad (16)$$

This last expression, in the Cole–Cole case, coincides with Eq. (15) of [21]. Eq. (16) of this present work could be extracted as well from Eq. (15) of Dygas work [21] with the help of our Eq. (11). However, it seems that an equation like our Eq. (16) has not been reported there, since the research work in Ref. [21] is concentrated between other things in the physical meaning of their modified BNN coefficient.

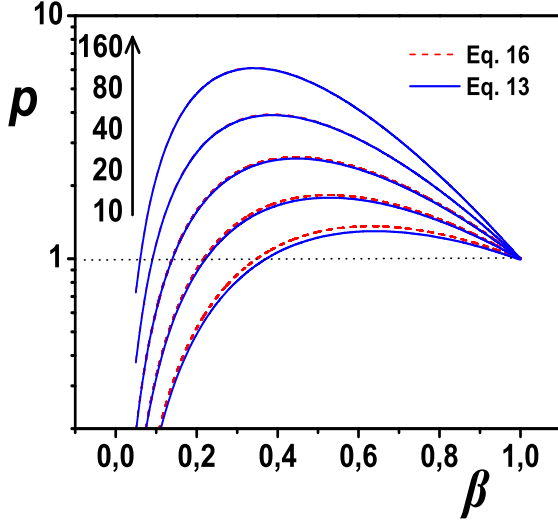


Figure 1: The BNN coefficient p as a function of H–N parameter β for different frequency ratios (10, 20, ..., 160) according to Eqs (13), (16). This figure represents the C–D behavior.

4 Discussion

A distinction of the analysis presented above for the extraction of both Eqs. (13) and (16), in relation to other conductive–system dispersion models which are dealing with BNN matters, is the use of the H–N dielectric function here. The H–N function should be considered as $\varepsilon''(\omega)$ conductive–system values. The fact, that the H–N function is included in the AC conductivity term, is a consequence of its definition. The coefficient of the BNN relation has been found to depend on the H–N parameters α, β and the frequency ratio ω_0/ω_{HN} in both Eqs. (13) and (16). The parameters α and β represent the width and the skewness of the dielectric loss, $\varepsilon_d''(\omega)$, when viewed in a $\log(\omega)$ plot, and also describe the distribution function of the relaxation times [32]. The ratio ω_0/ω_{HN} should be viewed equivalently as the ratio of two characteristic time lengths, t_{HN}/t_0 , where t_{HN} is the characteristic time length of the ionic polarization mechanism and t_0 is the respective one of the onset of AC conductivity.

In Figs. 1 and 2 the dependence of BNN coefficient p versus the shape parameters α, β is given, for various values of the frequency ratio ω_0/ω_{HN} according to Eqs. (13) and (16). Two characteristic cases could be observed there: the asymmetric Cole–Davidson (C–D) behavior (Fig.1) and the symmetric Cole–Cole (C–C) one (Fig.2). As it is shown in both figures, for a behavior close to Debye one, the BNN coefficient approaches 1. For particular values of the parameters α, β in both cases, the value of p increases by increasing the frequency ratio.

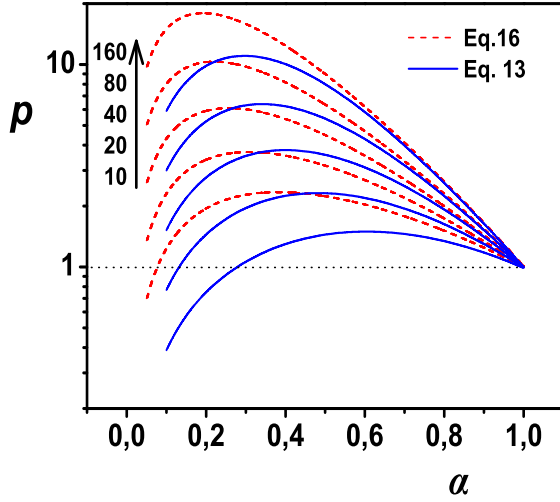


Figure 2: The BNN coefficient p as a function of H-N parameter α for different frequency ratios (10, 20, ..., 160) according to Eqs (13), (16). This figure represents the C-C behavior.

In both cases (C-D and C-C behavior) the value of p increases up to a maximum value as β or α decrease, and then p decreases as β or α continues to decrease. Values of $p < 1$ are allowed in Eqs. (13) and (16) for both behaviors. We observe also that for the majority of β or α parameter values, and for the ratios ω_0/ω_{HN} shown in Figs. 1 and 2 the p coefficient takes values between 0.2 and 10. As the ratio ω_0/ω_{HN} gradually decreases, the p coefficient tends to take values near unity.

As it can be seen in Fig. 1, the coincidence of the p coefficient values as specified by Eqs. (13) and (16) is excellent. Two different functions have identical behavior in C-D behavior; only for lower frequencies ratio ω_0/ω_{HN} is there little difference in the values of p , and this difference is less than 0.07. It is also apparent in Fig. 2 in the C-C behavior, that the values of p coefficient as provided by Eqs. (13) and (16) differ. But both p values are similar to the change as well the α parameter changes. The values of p coincide with each other to a greater range of high values of α parameter, as the frequency ratio increases in C-C case.

To clarify the discrepancy in symmetrical C-C behavior, it is necessary to present a representative simulation. For parameter values $\alpha = 0.4$, $\beta = 1$ and frequency ratio $\omega_0/\omega_{HN} = 40$, the values of BNN coefficient according to Eqs. (13) and (16) are found to be 3.78 and 5.38 respectively. Choosing the values $\sigma_0 = 10^{-6}$ S/m, $\omega_{HN} = \omega_{max} = 100$ rad/s and the requirement to satisfy Eq. (1), the extracted values are: $\Delta\varepsilon = 299$ from Eq. (13) and $\Delta\varepsilon = 210$ from Eq. (16).

The corresponding curves are presented in Fig.3 with different $\Delta\varepsilon$ values of Eq. (7) (with Eqs. (8), (9)).

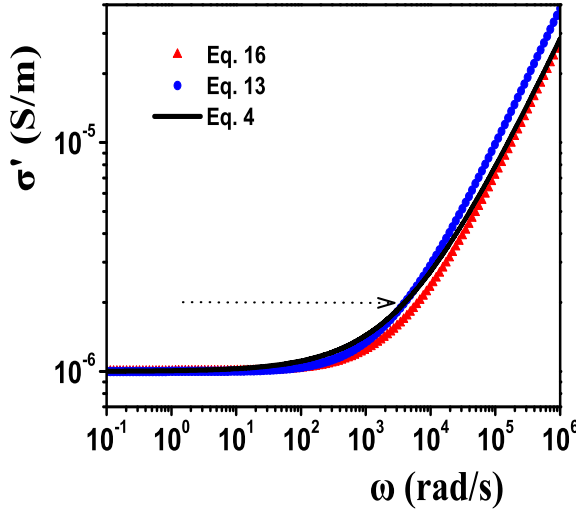


Figure 3: Simulation curves of the AC conductivity σ' as a function of ω (details in the text).

Also presented the corresponding Eq. (4) with $\sigma_0 = 10^{-6}$ S/m, $\omega_0 = 4000$ rad/s and $n = 0.6$ is also presented. It is clear that only the result of Eq. (16) produces a curve based on Eq. (7)(with Eqs. (8) and (9)), which is described very well by the Eq. (4) at low and high frequencies limits. The resulting $\Delta\epsilon$ as calculated using Eq. (13) fails to describe the power law frequency dependence of AC conductivity in the case of C-C dielectric behavior.

It should be noted here, that the additional assumption made in order to extract Eq. (13) is, that Eq. (4) and Eq. (7) (with Eqs. (8), (9)) should be equal (or at least approximate to a great extent), not only to high frequencies limit, but also at the characteristic frequency ω_0 . The failure of Eq. (13) in C-C dielectric behavior could possibly due to the fact that the previous additional assumption cannot be applied in these symmetric responses. As it is obvious in Fig. 3 the power law frequency dependence of AC conductivity as given by Eq. (4) differs substantially at $\omega = \omega_0$, with the one given by Eq. (7) with the aid of Eq. (16). In contrast, Eq. (7), based on the parameters of Eq. (13), although is not approximated well with power law (Eq. (4)) at the high frequencies limit seems to be approximated at frequency $\omega = \omega_0$ very well. The identification of p values in the asymmetric C-D behavior suggests that in these cases, the function $\sigma'(\omega)$ approximated well by Eq. (4) not only at the high frequency limit but also at frequency $\omega = \omega_0$. This should be the reason that the relations Eq. (13) and Eq. (16) although different, actually coincide in the prediction of BNN coefficient, in C-D behavior.

In what follows trying to achieve contact with real materials, we will refer to a case study of dielectric response of a crosslinked polyurethane (PUR) which satisfies the BNN relation. The $\epsilon''(\omega)$ experimental data of PUR [33] are fitted with a sum of H-N expression (Eqs. (8) and (9)) and the term $A\omega^{-k}$ which

represents the contribution of the DC conductivity, σ_0 , to the dielectric losses spectra with value of $k = 1$. A representative fit is shown at a temperature 363 K in Fig. 4. The dielectric dispersion exhibits, not only at this temperature, C-D behavior. The values of σ_0 were resolved from the extrapolation of low frequencies

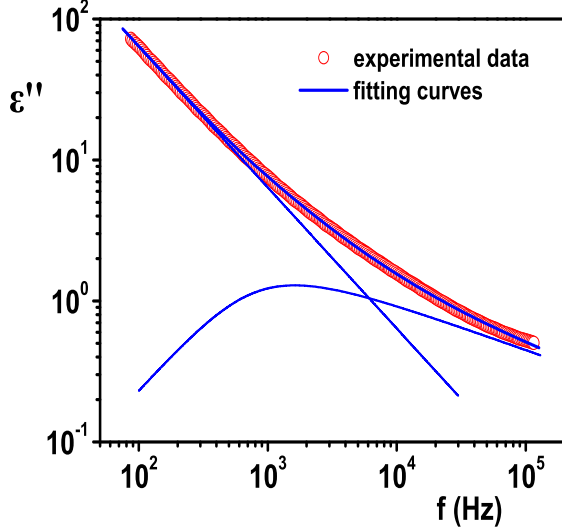


Figure 4: The imaginary part ε'' of the complex dielectric constant as a function of frequency f at a temperature 363 K for a crosslinked polyurethane. In the figure is shown the total fitting as well as the contribution of the polarization mechanism and the DC conductivity according to fitting process are shown.

$\sigma'(\omega)$ plateau at 1 mHz. The f_0 values ($\omega_0 = 2\pi f_0$) were taking these corresponding to values $2\sigma_0$ according to $\sigma'(\omega)$ data. It should be noted that the dipolar dispersions appear at higher enough frequencies [33] and so their contribution to $\varepsilon''(\omega)$ and $\sigma'(\omega)$ frequency spectrum studied here is negligible. Also during fitting process of $\varepsilon''(\omega)$ data, as well as the estimation of the DC conductivity, σ_0 , we have been restricted at a suitable low frequencies region, where the influence of the electrode effects could be considered as negligible. The parameter values resulting from the fitting process in $\varepsilon''(\omega)$ data, as well as the values of σ_0 and f_0 which have been calculated from $\sigma'(\omega)$ data are given in Table 1.

Experimental data of $\sigma'(\omega)$ are presented in Fig. 5. In the same figure, the simulation curves of Eq. (4) and Eq. (7) (with Eqs. (8), (9)) are shown according to the parameters values of Table 1. Despite the fact that Eq. (4) does not describe adequately the behavior of the rest two curves near the onset region of AC conductivity, there is a very good match in all curves for frequencies $\omega \geq \omega_0$.

The values of the coefficient p , as calculated based on the predictions of Eq. (13) and Eq. (16) as well as on the BNN relation, Eq. (1), are presented in Table 2. In order to do these calculations the corresponding values contained in Table 1 have been used. Although the temperature window is relatively small, it is evident

Table 1: The parameter values of α , β , $\Delta\epsilon$ and f_{HN} resulting from the fitting process in $\epsilon''(\omega)$ data as well as the values of σ_0 and f_0 for crosslinked polyurethane at different temperatures T . We consider that the values of σ_0 and f_0 have been estimated with high accuracy and therefore those are given without errors.

$T(K)$	α	β	$\Delta\epsilon$	f_{HN} (Hz)	f_{max} (Hz)	f_0 (Hz)	σ_0 (S / m)
323	1 ± 0.00	0.39 ± 0.01	4.9 ± 0.1	62 ± 5	132 ± 11	560	3.50×10^{-8}
333	1 ± 0.00	0.37 ± 0.01	4.8 ± 0.1	123 ± 5	272 ± 11	1185	7.00×10^{-8}
343	1 ± 0.00	0.34 ± 0.01	4.9 ± 0.1	198 ± 7	470 ± 17	2178	1.27×10^{-7}
353	1 ± 0.00	0.33 ± 0.01	4.8 ± 0.1	367 ± 11	894 ± 27	3560	2.15×10^{-7}
363	1 ± 0.00	0.33 ± 0.01	4.7 ± 0.1	656 ± 20	1597 ± 48	5501	3.48×10^{-7}

that p coefficient shows a gradual reduction, with increasing temperature, in all calculations included in Table 2. The change of p , throughout the temperature range, appears to be 0.15–0.19. At each temperature the p values as they have been calculated using the three equations, show an excellent agreement at all temperatures. According to this analysis, in order for the coefficient p to be temperature independent, the

Table 2: The values of p coefficient at various temperatures.

$T(K)$	p (Eq. (16))	p (Eq. (13))	p (Eq. (1))
323	1.04 ± 0.05	0.97 ± 0.06	0.98 ± 0.07
333	1.03 ± 0.03	0.97 ± 0.03	0.97 ± 0.04
343	1.05 ± 0.03	0.99 ± 0.03	0.99 ± 0.03
353	0.93 ± 0.02	0.88 ± 0.02	0.90 ± 0.03
363	0.85 ± 0.02	0.79 ± 0.02	0.83 ± 0.03

parameters α , β and ω_0/ω_{HN} must be temperature independent, or in the case that they are temperature dependent, their contributions on p value must be such that they cancel each other. In any other case the coefficient of p is expected to be temperature-dependent.

In Ref. [21], experimental data have been mentioned, which are relevant to Havriliak–Negami dielectric function and the characteristic frequency ratio in three different systems which satisfy the BNN relation. The BNN coefficient is calculated according to original BNN relation, and it has been found that it is equal to 7.1, 1.34 and 2.1 for a single crystal, a type of glass and a PEO polymer electrolyte respectively (for details see Table 1 of Ref. [21]). Based on the values of Table 1 of Ref. [21], the BNN coefficient was found to be 4.6, 1.15 and 1.7 by using Eq. (13), while by using Eq. (16) it was found to be 4.8, 1.32 and 2.1 for a single crystal, glass and PEO polymer electrolyte respectively. We observe that the values found using Eq. (16) are identical to those based on the original BNN relation for glass and PEO polymer electrolyte, while those of Eq. (13) result in values close enough as well. However, in the case of the single crystal, although Eq. (13) and Eq. (16) result in very close values, these values differ significantly from the one extracted using the original BNN relation. This difference is possibly due to uncertainties during the fitting process. The fitting of Havriliak–Negami function in $\epsilon''(\omega)$ and $\epsilon'(\omega)$ data after subtraction of the DC conductivity and electrode effects respectively, lead generally in scattering of the data points at frequencies lower than the ones which correspond to the peak of the dielectric dispersions. This fitting process has as a result uncertainties in the estimation of the Havriliak–Negami parameters.

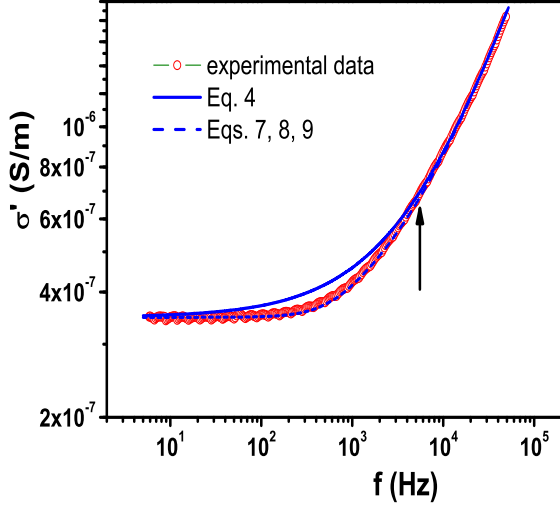


Figure 5: The AC conductivity σ' as a function of frequency f at 363 K for a crosslinked polyurethane. The lines correspond to simulation curves according Eq. (4) and Eqs. (7), (8), (9), and using the corresponding values of Table 1.

As can be seen observing the values of Table 1, the relation in Eq. (15) is satisfied with sufficient accuracy. Note here that the strength of this relationship requires the power law Eq. (4) to approach very well the function $\sigma'(\omega)$ only at the higher frequencies limit, and thus its validity is more general. From Eq. (13) and Eq. (16) is evident that there are many possible p values. Also, for a given value of BNN coefficient, there are several possible combinations of parameters α , β , and ω_0/ω_{HN} , according to Eqs. (13) and (16). In these cases, not only the high frequencies slope of function $\sigma'(\omega)$, but also the ratio $\sigma_0/\omega_0\Delta\epsilon$ could be different with consequences in scaling diagrams of AC conductivity. Of course one question is if all these different combinations of parameters may correspond to the response of the real materials. Assume for simplicity that the ionic polarization mechanisms of a category of materials, characterized by particular values α , β and ω_0/ω_{HN} . Then, these materials characterized by a single value of p . This seems to be compatible with the universal value of p , as proposed by Macdonald [18] for ion-conducting glasses and single crystals. His conclusion is based on the observation that these materials are characterized by the same shape parameter β_{1C} of KWW response function and also the same characteristic frequencies ratio of K1 model. This indicates that H-N and KWW shape parameters are closely related, as well as the characteristic frequencies ratio of our approach (ω_0/ω_{HN}) to that of the K1 model. Particular values of the parameters α , β and ω_0/ω_{HN} implies that the corresponding materials not only have same p value but also have the same ratio $\sigma_0/\omega_0\Delta\epsilon$, according to Eq. (15). Of course there are many possible combinations of σ_0 , ω_0 and $\Delta\epsilon$ values which keep this ratio constant. But only some of these combinations correspond to the response of real materials.

In a recent paper Dyre *et al.* [22] applied the fluctuation-dissipation theorem in ionic conductors.

According to their calculations, the DC conductivity is

$$\sigma_0 = \frac{n(t_0)q^2}{6k_B T} \frac{\langle \Delta r^2(t_0) \rangle}{\gamma H} \omega_0, \quad (17)$$

where q denotes the ions charge, k_B is the Boltzmann constant, T is the absolute temperature, $n(t_0)$ is the number density of mobile ions at time $t_0 = 1/\omega_0$ (ω_0 being the onset frequency), $\langle \Delta r^2(t_0) \rangle$ is the single-particle mean square displacement, while γ and H are numbers which are roughly of order one. Roling *et al.* [34] using linear response theory have found a relation between the ionic dielectric strength, $\Delta\varepsilon$, and the mean-square displacement of the center of the mobile ions, $\langle \tilde{R}^2(\infty) \rangle$, in ionic glasses conductors

$$\varepsilon_0 \Delta\varepsilon = \frac{N_V q^2}{6k_B T} \langle \tilde{R}^2(\infty) \rangle, \quad (18)$$

where N_V is referred as the number density of mobile ions. Similar expressions to that of Eq. (18) have already been reported in the literature [23, 35]. Now, substituting the quantity ω_0/σ_0 as given by Eq. (17) and that of $\varepsilon_0 \Delta\varepsilon$ as given in Eq. (18), back into Eq. (15), we arrive at the following expression

$$\frac{\omega_0}{\omega_{HN}} = \frac{t_{HN}}{t_0} = \left[\gamma H \sin\left(\frac{\alpha\beta\pi}{2}\right) \frac{N_V}{n(t_0)} \frac{\langle \tilde{R}^2(\infty) \rangle}{\langle \Delta r^2(t_0) \rangle} \right]^{\frac{1}{\alpha\beta}}. \quad (19)$$

The factor $\gamma H \sin(\alpha\beta\pi/2)$ in the previous equation takes values close to unity, for typical broad ionic dispersions. The characteristic frequencies or times ratio depends on the number densities of mobile ions at different time scales which characterize the AC response, as well as to the corresponding distance lengths of ions motion. The other factor affecting the characteristic ratio is the product $\alpha\beta$ which represents the high frequency absolute slope of ionic dispersion in $\log \varepsilon_d''$ vs. $\log \omega$ plot, and it is connected to the high frequency limiting response power law exponent of σ' . The lower the value of $\alpha\beta$, the stronger its influence on the characteristic ratio is. As a consequence of this, different values of the power law exponent in the high frequency limit of AC conductivity, lead to different values of BNN coefficient, in accordance with the conclusions about the non-universality of p value, as has been suggested by Hunt [20]. From Eq. (19), which is based on two different models [22, 34], it is obvious that particular values of α , β and ω_0/ω_{HN} correspond to a specific correlation of the number densities as well as of the distance length of mobile ions at different time scales, which affect the macroscopic characteristic of long and short range ions motion.

Finally, it should be noted that the high frequency slope of σ' , is $n = 1 - \beta_{KWW}$, where β_{KWW} is the corresponding KWW stretched exponential parameter [36, 37]. So, according to the present analysis $\beta_{KWW} = \alpha\beta$, where α and β represent the H-N shape parameters of the ionic polarization mechanism in ε^* formalism. The connection between the H-N and KWW parameters appears also in other relevant works in the literature [32, 38, 39].

5 Conclusions

Summarizing this work, the BNN relation has been extracted while it has been found that p coefficient depends on the H-N shape parameters α and β as well as on the ratio ω_0/ω_{HN} of two frequencies which

are directly connected to characteristic time scales of ions motion (Eq.(13)). This equation is compared to the BNN relation (Eq.(16)) which could be extracted based on Dygas findings in his previous work. Both approaches highlight the dependence of BNN coefficient from the same parameters. In C–D dielectric behavior of ionic polarization mechanism, both relationships are nearly identical predictions with very high accuracy for the p coefficient, while deviations are observed in the C–C one. Representative simulations have shown that only Eq.(16), is consistent with the power law frequency dependence of AC conductivity in symmetrical C–C cases. The identification of p values in asymmetric C–D behavior indicates that in these cases, the function $\sigma'(\omega)$ should be approached very well from the power law not only at high frequency limit but also at $\omega = \omega_0$. Both expressions of BNN relation could result in many possible p values. However, the response of matter could exhibit individual characteristics. In both cases, of C–D and C–C behavior, the p values, depending on ω_0/ω_{HN} ratio, lie within the range where the majority of the p values recorded in the literature falls. Specifically, p values close to unity arise for the lower values of the ratio ω_0/ω_{HN} and for an appreciable range of the H–N shape parameters β and α .

The two expressions of BNN coefficient, applied to experimental data of a crosslinked polyurethane, which satisfies the BNN relation and the ionic polarization mechanism exhibits C–D behavior. Both predictions are in excellent agreements with the values calculated from original BNN relation, according to experimental data analysis. The results also showed a trend of gradual reduction of the p coefficient, as the temperature increases.

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